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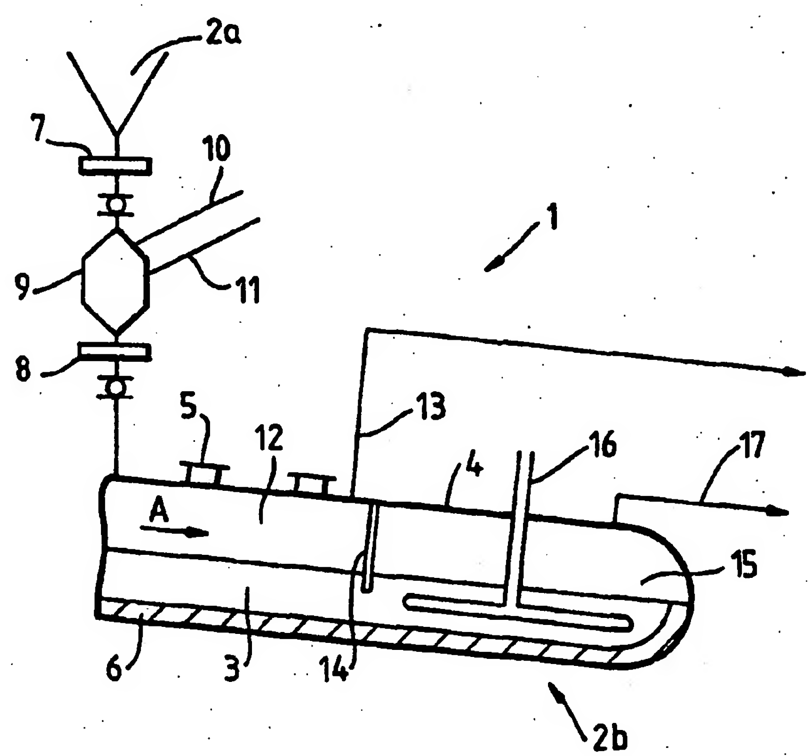
(54) Title: THERMAL TREATMENT OF CARBONACEOUS MATERIAL

(57) Abstract

Carbonaceous materials are heated by microwave radiation in a first zone having an atmosphere in which flame generation is substantially prevented, and then part of the hot carbonaceous material is moved into a second zone where thermal energy is released to a heat exchanger, the thermal energy being latent or generated by combustion of the material in the second zone. Apparatus comprises a housing with first (3) and second (4) zones, a microwave radiation source (5), a gas barrier (14) between the zones, and a heat exchanger (16) in the second zone (4).



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THERMAL TREATMENT OF CARBONACEOUS MATERIAL

The present invention is concerned with the thermal treatment of carbonaceous material, such as carbonaceous waste materials.

It is known to dispose of waste materials by heating them to effect thermal degradation. This can be carried out in conventionally heated furnaces or, more commonly in recent times, by using microwave radiation. Waste materials which are not themselves susceptible to microwave radiation, can be treated by contacting them with microwave-heatable materials such as carbonaceous materials. These processes are described in my PCT patent applications nos. WO 88/08871, WO 89/04355 and WO 92/02598 to which reference should be made for further details.

In these processes, either the heating medium itself or the product of the pyrolysis or both, comprise carbon and in the treatment of scrap material on a continuous basis, the amount of carbon builds up. Normally, it is either recycled or it is treated to remove materials such as metals, and it is then disposed of to waste. In many of the known processes, the gaseous pyrolysis products are recycled or otherwise treated to maintain the energy balance and reduce the overall cost of treating the waste.

We have now found that further very substantial economies can be achieved by modifying the known processes so that the hot carbon is removed from the microwave zone directly to a second zone in which heat-exchange is

effected. In this way, significant advantages can be obtained.

According to the present invention, there is provided a method of thermal treatment of carbonaceous material, which comprises

(a) thermally treating a medium comprising carbonaceous material by means of microwave radiation in a first zone having an atmosphere under which flame generation is substantially prevented;

(b) causing at least part of the treated medium to flow to a second zone; and

(c) heating heat-exchange means directly or indirectly in the second zone by means of the medium.

In step (c), the hot medium may be contacted directly with the heat exchange means in an non-oxidising atmosphere, or oxygen can be present in which case thermal energy is released by combustion of the hot medium.

According to a first aspect of the present invention, the medium consists essentially of carbonaceous material; the latter may consist essentially of elemental carbon, or it may be capable of being pyrolysed to elemental carbon by microwave radiation.

According to a second aspect of the present invention, the medium contains carbonaceous material as hereinbefore described admixed with a secondary material not itself susceptible to microwave heating. The nature of the secondary material is such that contact of the material with hot elemental carbon can yield heat from the former. The contact of the carbon and secondary material may merely involve heat transfer from the former to the latter; alternatively the contact may involve a chemical interaction therebetween. A preferred secondary material includes metal ores susceptible to reduction by hot carbon, for example zinc or aluminium ores. In this way, metals can be obtained from the process.

The carbonaceous material typically comprises

waste hydrocarbon or carbohydrate material. Examples of such materials include natural or synthetic rubber compounds (which may be pyrolysable to elemental carbon by microwave radiation), agricultural waste material such as citrus fruit peel, olive waste products and nut shell, non-putrescent domestic waste, toxic waste, hospital waste and halogenated hydrocarbons, or other types of organic refuse.

In some embodiments (and particularly where the material being thermally treated is a rubber compound), it is preferred that the carbonaceous material should contain carbon filler. A particularly preferred carbonaceous material is carbon-filled vulcanised rubber, such as a waste tyre compound in chopped or finely divided form.

The thermal treatment of the medium typically involves pyrolysis of the carbonaceous material, whereby fission of carbon-carbon bonds, and of more polar chemical bonds, yields elemental carbon which can then be fed or passed to the second treatment zone. The thermal treatment involves heat transfer or chemical interaction between the carbonaceous material and any secondary material not susceptible to microwave heating, such as the reduction of metal ores as hereinbefore described.

The microwave radiation is preferably employed at such a power and for sufficient time as to effect the above described pyrolysis of the carbonaceous material, and, where appropriate, also treatment of the secondary material as described above. Typically the temperature of the medium in the first zone is from about 800°C upwards.

Typically the microwave radiation is supplied to the first zone by means of at least one, preferably more than one, microwave generators. In the case where a plurality of generators are employed, the generators may be of similar power output, or, alternatively of graduated power output (for example, of gradually increasing or decreasing power output in the downstream direction). It is preferred that the microwave generators operate at a power

output in the region of 60kw.

The atmosphere of the first zone is preferably substantially oxygen-free. Preferably the atmosphere is reducing, typically comprising a hydrocarbon medium, or an inert gaseous medium such as nitrogen. It is preferred to use a reducing atmosphere when environmentally sensitive compounds, such as halogenated compounds and sulphur are expected in the gas products (for example when the material being treated comprises CFC's, PCB's or mercaptans). These compounds would therefore be converted to acids (HF, HCl, HBr, H_2S) which can be readily scrubbed from the exhaust gases.

It is further preferred that the atmosphere of the first zone is self-perpetuating, whereby pyrolysis of the waste material during microwave radiation yields hydrogen and low molecular weight gaseous hydrocarbons from the carbonaceous material, so as to provide a reducing atmosphere in the first zone.

The gaseous hydrocarbon products produced in thermal treatment step (a) are preferably recycled, the recycled hydrocarbon products optionally being mixed together with other air-excluding gases, such as carbon monoxide or carbon dioxide. The recycling is advantageous in lessening the requirement for separate supply of gaseous hydrocarbons, and is also beneficial in the following instances:

(i) where a decrease in the partial pressure of condensible products of thermolysis is required, in order to preclude condensation (in this case, the recycled hydrocarbon stream would be cooled, condensate removed and the stream re-heated);

(ii) where a carrier gas is required to remove products from the treatment zones; and

(iii) where an increase in partial pressure of hydrogen is required to strengthen the reducing power of the atmosphere of the first zone.

The heat exchange means are in the second zone, so that a heat exchange fluid can be heated. Typically the heat exchange fluid comprises water or air, or any other fluid which can be heated in a substantially controlled fashion. Heating water to form steam is preferred.

It is further preferred that exit means are provided for transfer of thermal energy generated in the method to a heat exchange apparatus or the like, where its thermal properties can be utilised to generate heat in a heating system. It is further preferred that gaseous outlet means are provided, for transfer of hot gaseous by-products to heat exchange apparatus according to the invention.

In a preferred embodiment, the second zone contains an atmosphere which promotes combustion of hot elemental carbon. Typically the second zone atmosphere comprises an oxygen-containing medium, the oxygen preferably being present at a level of at least about 5% by volume.

It is preferred that gaseous communication between the first and second zones is substantially precluded. Preferably baffle means or other gas precluding means, such as air locks or the like, are provided between the first and second zones for this purpose.

The method is typically carried out in a thermally resistant housing which is preferably resistant to temperatures of up to about 1800-2000°C. The housing may typically be of fire brick-lined or refractory-lined, stainless steel or ceramic material.

In a first embodiment of the invention, it is preferred that step (b) of the method involves feeding the thermally treated medium along an inclined transfer surface arranged to communicate between the first and second zones. Typically, the medium is allowed to flow along the inclined surface, under the influence of gravity, from the first zone to the second zone.

The medium may be fed, typically by means of a gravity feed hopper, into the first zone, to be collected on

the transfer surface. The first zone may comprise an inner, substantially circular chamber, in which case the second zone preferably comprises a circumferential annular chamber arranged around the inner chamber. Preferably, the transfer surface is defined by the floor of the chambers, and typically provides a substantially conical or frustoconical surface over which the carbonaceous material can flow. Typically the medium is fed to an apex region of the conical transfer surface.

In a second embodiment, the first and second zones respectively comprise first and second chambers, arranged such that the first chamber is superjacent the second chamber. The carbonaceous material can sink through the first chamber, such that at least part of the treated medium is passed to the second chamber.

The chambers in the second embodiment may be arranged remote from one another, communication between the remote chambers being provided by a conduit arranged to extend therebetween. The conduit may be provided with an air lock for precluding gaseous communication between the chambers.

Alternatively, the superjacent first chamber may be at least partly enclosed by the second chamber, such that the treated material can be allowed to sink directly from the first chamber to the second chamber.

There is further provided by the present invention apparatus for thermally treating a medium comprising a carbonaceous material, which apparatus comprises:

(a) a housing comprising first and second zones, which zones are arranged such that at least part of the medium can flow directly from the first zone to the second zone;

(b) at least one microwave radiation source arranged so as to be capable of directing microwave radiation into the first zone to thermally treat the medium;

(c) means for substantially precluding gaseous communication between the zones; and

(d) heat exchange means provided for the second zone, such that the means can be directly or indirectly heated in the second zone by at least part of the thermally treated medium.

The parts of the apparatus according to the invention may be substantially as hereinbefore described with reference to the method according to the invention.

The present invention further comprises a heating system, which comprises:

(i) apparatus according to the invention;

(ii) thermal storage means; and

(iii) a heat exchange system arranged to convey heat generated in said apparatus to said thermal storage means.

One highly preferred aspect of the present invention comprises a method of thermal treatment of waste material not susceptible to microwave radiation, which comprises contacting the waste material, in a first zone under an atmosphere where flame generation is substantially prevented, with a bed of pulverulent material which comprises carbon in elemental form, or a material which is capable of being pyrolysed to elemental carbon by microwave radiation; and heating the pulverulent material by means of microwave radiation such that thermal energy is transferred to the waste material to pyrolyse it to carbon; and wherein carbon is removed from the first zone to a second zone and immediately treated to release thermal energy therefrom for recovery by a heat-exchange medium.

In this method, operated on a continuous basis, carbon is formed in the first zone and thus, to prevent a build-up, some carbon is removed continuously or intermittently. According to the present invention, the utilisation of this carbon to release thermal energy is a surprising and highly advantageous concept since the material would otherwise not be utilised to release energy.

The energy can be released by direct heat exchange or by permitting combustion in the second zone, to release further heat.

The invention will now be further illustrated with reference to the accompanying drawings, like parts being denoted by like numerals, wherein:

Figure 1 is a schematic representation of a portion of a first embodiment of apparatus according to the present invention;

Figure 2 is a schematic representation of a second embodiment of apparatus according to the present invention; and

Figure 3 is a schematic representation of a modification of the apparatus of Figure 2.

Referring to Figure 1, there is shown apparatus generally designated 1 which comprises a feeder 2a and a treatment vessel 2b. Treatment vessel 2b comprises a reducing chamber 3 and a circumferentially extending oxidising chamber 4.

Although not fully shown in the drawing, reducing chamber 3 comprises an inner circular zone of vessel 2b, and oxidising chamber 4 comprises a circumferential annular chamber around chamber 3.

A plurality of microwave generators 5 are arranged relative to treatment vessel 2b so as to be capable of directing microwaves into the reducing chamber 3. The microwave generators 5 may all be of substantially similar power output, or alternatively, of graduated power output (for example, of gradually increasing or decreasing power in the direction of travel of material to be pyrolysed through chamber 3 as shown by arrow A).

Transfer surface 6 is inclined so that elemental carbon present in chamber 3 can flow to oxidising chamber 4.

Feeder 2a is arranged above chamber 3, so that any waste material contained in feeder 2a can be allowed to fall

onto transfer surface 6 within chamber 3. Feeder 2a comprises first and second valve members 7 and 8, for controlling discharge of waste material from feeder 2a. Feeder 2a includes an intermediate chamber 9, in which waste material to be treated can be stored if required.

Intermediate chamber 9 is provided with first and second vacuum pumps 10 and 11, wherein vacuum pump 10 is in gaseous communication with the external atmosphere and vacuum pump 11 is in gaseous communication with a hydrocarbon gaseous recycling system of the apparatus (the recycling system not being shown in the drawing).

The material to be treated in apparatus 1 comprises a waste material comprising, or pyrolysable to, elemental carbon.

The waste material is fed into chamber 3 via feeder 2a. Although feeder 2a is shown as a gravity fed mechanism, it is of course appreciated that the waste material could be fed to chamber 3 in a number of ways, such as an inclined slope feeding mechanism, a substantially horizontal feed conveyor or the like.

On arrival in chamber 3, the waste material is subjected to microwave radiation for a sufficient time and intensity so as to convert the material to a medium consisting essentially of elemental carbon. Chamber 3 contains an atmosphere 12 under which flame generation is substantially prevented, and typically comprises a nitrogen or hydrocarbon reducing gaseous medium. Atmosphere 12 is self-perpetuating, in that pyrolysis of the waste material during the microwave radiation, yields low molecular weight gaseous hydrocarbons from the waste material.

The temperature of material being pyrolysed will depend on the material itself and may range, for example, from about 800°C upwards, as will be clear to those skilled in the art. A common temperature range is 800° to 1200°C but higher temperatures can certainly be used depending on the material being treated.

Although not shown in the diagram, chamber 3 is provided with a gas inlet for communicating at least the initial reducing atmosphere to chamber 3. Outlet 13 provides an exit for gaseous hydrocarbon by-products which are transmitted to condensation or distillation processing systems (not shown). Baffle 14 is provided to obviate gaseous communication between chambers 3 and 4.

Following pyrolysis of the waste material to elemental carbon in chamber 3, the elemental carbon medium is conveyed to chamber 4. Chamber 4 can have a non-oxidising inert atmosphere so that mere heat exchange is effected. However, it can instead contain an oxygen-rich atmosphere 15. Inlet 16 is provided to communicate an oxygen rich gas to chamber 4, and outlet 17 is provided for removing hot combustion gases from chamber 4. On contact of the elemental carbon with atmosphere 15, the former combusts to yield hot gaseous products which escape chamber 4 via outlet 17.

Outlet 17 conveys the hot gaseous products to a heat exchange apparatus or the like, where their thermal properties can be utilised to generate heat in a heating system.

Heat exchange apparatus (not shown) are provided in chamber 4, so that a heat exchange fluid, such as water, can be directly or indirectly heated in chamber 4 by means of the hot elemental carbon.

Referring to Figure 2, there is shown apparatus generally designated 1 which comprises a feeder 2a, a reducing chamber 3 and a subjacent oxidising chamber 4.

A microwave generating source 5 is arranged to direct microwaves along conduit 18 into reducing chamber 3. Conduit 18 is provided with a pressure resistant microwave window 19.

Feeder 2a is provided with first and second vacuum pumps 10, 11 as described with reference to Figure 1. Outlet 13 provides an exit for gaseous hydrocarbon by-

products which are transmitted to condensation or distillation apparatus.

Conduit 20 extends between the base portion 3a of chamber 3 and the top portion 4a of chamber 4. Conduit 20 is provided with an air lock 21 for precluding gaseous communication between chambers 3 and 4.

Chamber 4 is provided with an inlet 16 for supply of an oxygen-rich gas and outlet 17 is provided for the removal of hot combustion products from chamber 4. Outlet 17 conveys the hot gaseous products to heat exchange apparatus.

The gaseous supply and temperature conditions within chamber 4 are such that a fluidised bed combustor is provided therein.

In use, the carbonaceous material is fed to chamber 3 and is pyrolysed to yield elemental carbon. The treated medium, which is rich in elemental carbon, is allowed to sink through chamber 3 and conduit 20, so as to be transferred to the oxygen-rich environment of chamber 4.

Referring to Figure 3, it can be seen that the arrangement of chambers 3 and 4 is similar to that in Figure 2.

However, Figure 3 shows chamber 3 as comprising a receptacle 22 having an open end 23. Chamber 4 is arranged to circumferentially enclose the main body 24 of receptacle 22.

In use, the carbonaceous material is pyrolysed in receptacle 22, the treated medium sinks through receptacle 22 and is passed through open end 23 to chamber 4.

CLAIMS:

1. A method of thermal treatment of carbonaceous material, which comprises
(a) thermally treating a medium comprising carbonaceous material by means of microwave radiation in a first zone having an atmosphere under which flame generation is substantially prevented:
(b) causing at least part of the treated medium to flow to a second zone; and
(c) heating heat-exchange means directly or indirectly in the second zone by means of the medium.

2. A method according to claim 1, wherein the medium consists essentially of elemental carbon or of a material capable of being pyrolysed to elemental carbon by microwave radiation.

3. A method according to claim 1, wherein the medium also comprises a secondary material not susceptible to microwave heating.

4. A method according to claim 3, wherein the secondary material comprises a metal ore reducible by hot carbon, or waste plastics material.

5. A method according to any of claims 1 to 4, wherein the carbonaceous material comprises waste hydrocarbon or carbohydrate materials.

6. A method according to any of claims 1 to 5, wherein in the first zone a reducing atmosphere is maintained.

7. A method according to any of claims 1 to 6, wherein the second zone is immediately adjacent the first zone.

8. A method according to any of claims 1 to 7, wherein in step (c) the medium is oxidised to release heat.

9. A continuous method of thermal treatment of waste material not susceptible to microwave radiation, which comprises contacting the waste material, in a first zone under an atmosphere where flame generation is substantially prevented, with a bed of pulverulent material which comprises carbon in elemental form, or a material which is capable of being pyrolysed to elemental carbon by microwave radiation; and heating the pulverulent material by means of microwave radiation such that thermal energy is transferred to the waste material to pyrolyse it to carbon; and wherein carbon is removed from the first zone to a second zone and immediately treated to release thermal energy therefrom for recovery by a heat-exchange medium.

10. A method according to claim 9, wherein the second zone is adjacent the first zone, and thermal energy is released either by direct contact or by oxidising the carbon in the second zone.

11. A method according to claim 9 or 10, wherein the waste material is plastics material, municipal solid waste and/or biomedical waste.

12. Apparatus for thermally treating a medium comprising carbonaceous material, which apparatus comprises:
(a) a housing comprising first and second zones, which zones are arranged such that at least part of the medium can flow directly from the first zone to the second zone;
(b) at least one microwave radiation source arranged so as to be capable of directing microwave radiation into the first zone to thermally treat the medium;
(c) means for substantially precluding gaseous

communication between the zones; and

(d) heat exchange means provided for the second zone such that the means can be directly or indirectly heated in the second zone by at least part of the thermally treated medium.

Fig.1.

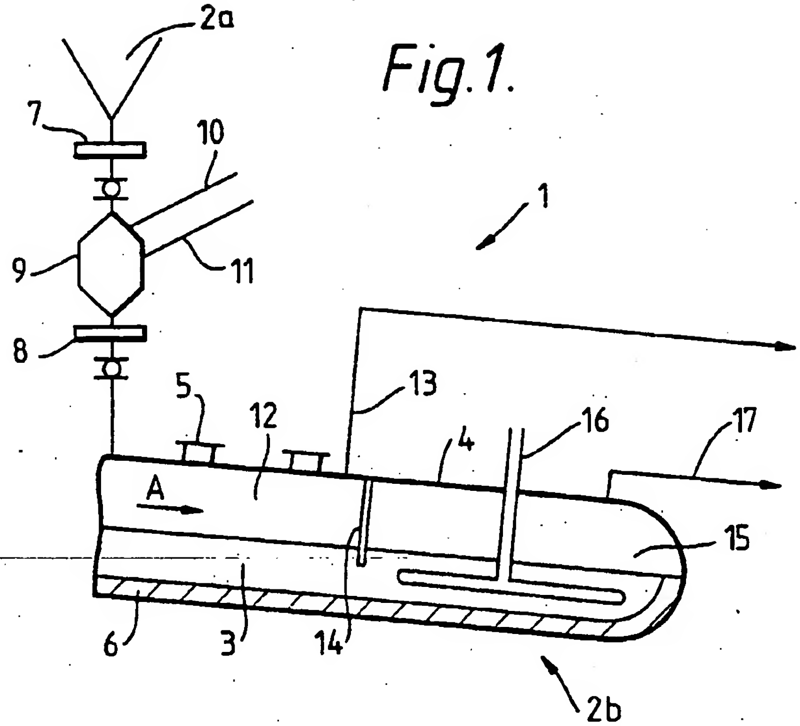


Fig.3.

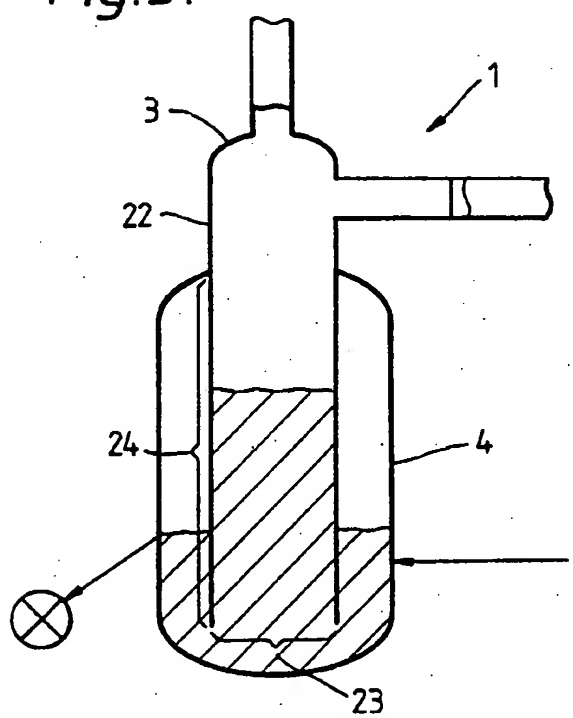
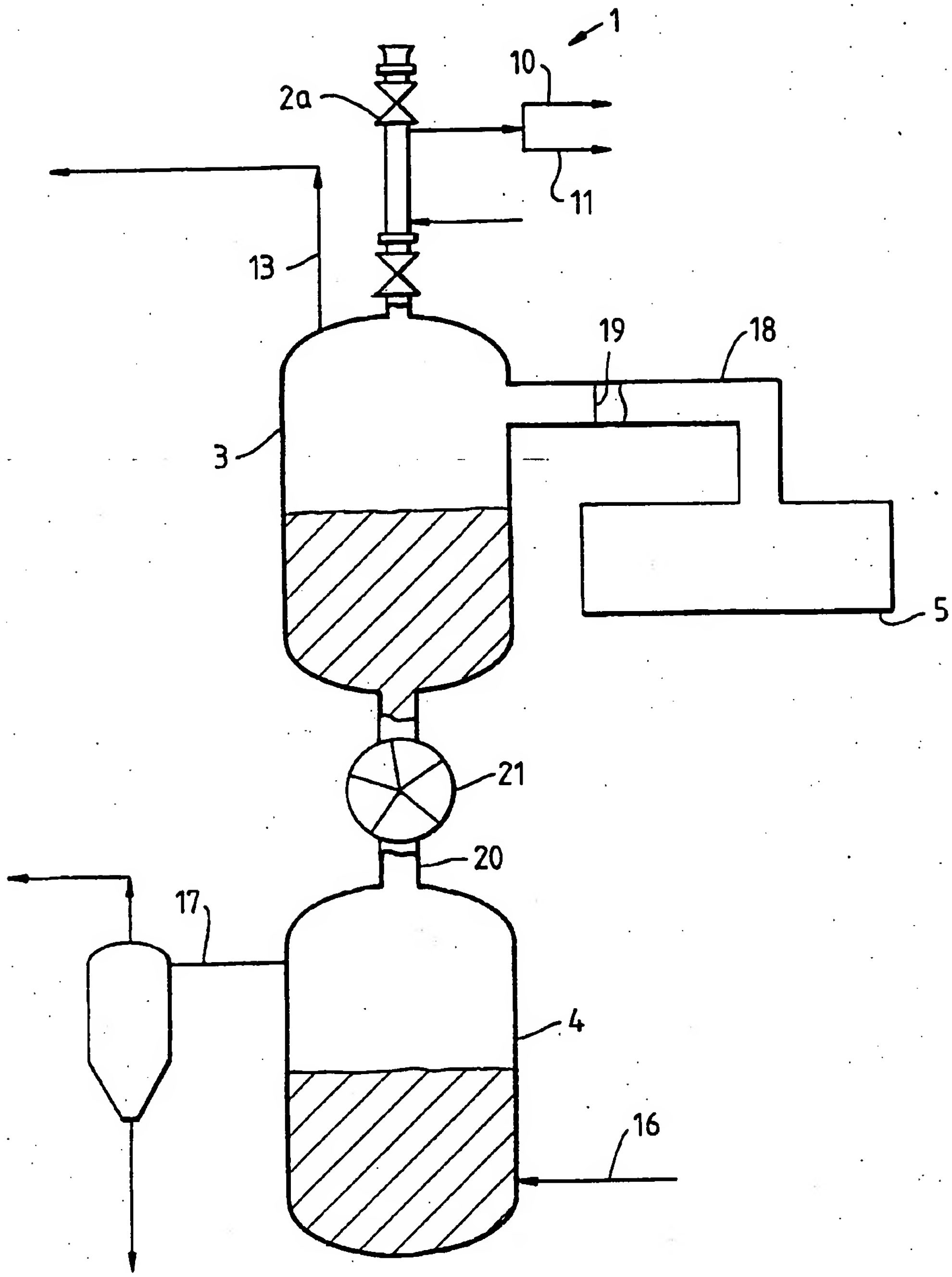


Fig.2.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/00205

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C10B53/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C10B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB,A,1 562 492 (FOSTER WHEELER) 12 March 1980	
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A	WO,A,89 04355 (HOLLAND) 18 May 1989 cited in the application	
A	WO,A,92 02598 (HOLLAND) 20 February 1992 cited in the application	

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 May 1994	30.05.94

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Information on patent family members

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